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USPT	(multi or mixed or mixture) adj3 (l11)	71	<u>L15</u>
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USPT	l9 and l11	34	<u>L13</u>
USPT	l9 and l10	27	<u>L12</u>
USPT	(melt adj flow adj index) or (MFI)	4516	<u>L11</u>
USPT	melt adj flow adj index	3321	<u>L10</u>
USPT	l3 same l6	244	<u>L9</u>
USPT	l5 and l6	6	<u>L8</u>
USPT	l5 and l4	87	<u>L7</u>
USPT	bimodal or multimodal	3506	<u>L6</u>
USPT	l4 and l2	87	<u>L5</u>
USPT	l1 same l3	1488	<u>L4</u>
USPT	polyolefin or polyethylene or polypropylene	291667	<u>L3</u>
USPT	fluoropolymer	5808	<u>L2</u>
USPT	(processing or process) adj (aid or agent)	11174	<u>L1</u>

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L8: Entry 6 of 6

File: USPT

Feb 17, 1998

DOCUMENT-IDENTIFIER: US 5718974 A

TITLE: Cable jacket

**BSPR:**

It will be understood that generally the in situ blend can be characterized as a multimodal resin, usually bimodal or trimodal. In some cases, however, the two components making up the blend are sufficiently close in average molecular weight that there is no discernible discontinuity in the molecular weight curve.

**DETL:**

TABLE VI \_\_\_\_\_ Standard Test Formulation (in percent by weight) \_\_\_\_\_ Base polyethylene resin  
92.21 Carbon Black Masterbatch 7.50 Antioxidant I 0.20 Antioxidant II 0.07  
Fluoropolymer processing aid 0.02 Total 100 percent

Notes to Table VI: 1) Carbon black masterbatch contains 35 percent furnace black; 0.2 percent Antioxidant III; and 65 percent LLDPE having a melt index of 0.65 gram per 10 minutes and a density of 0.920 gram per cubic centimeter. 2) Antioxidant I is polymerized 2,2,4-trimethyl-1,2-dihydroquinoline. 3) Antioxidant II is thiodiethylenebis(3,5-di-tert-butyl-4-hydroxy)-hydrocinnamate. 4) Antioxidant III is 4,4'-thio bis(6-tert-butyl-3-methylphenol).

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L13: Entry 1 of 34

File: USPT

Jul 18, 2000

DOCUMENT-IDENTIFIER: US 6090893 A  
TITLE: Polyethylene composition

**ABPR:**

The invention relates to polyethylene compositions containing 85-99.5 weight % of component A, which is a linear (co)polymer of ethylene having a bimodal weight distribution, and 0.5-15 weight % of component B having a unimodal molecular weight distribution. Component A is 40-60% by weight of a low molecular weight component (A1) having a weight average molecular weight between 5,000 and 50,000 g/mol, and a molecular weight distribution Mw/Mn between 2.5 and 9 and 60-40% by weight of a high molecular weight component (A2) having a weight average molecular weight between 300,000 and 900,000 g/mol, and a molecular weight distribution M/w/Mn between 4.5 and 12. Component B is a linear ethylene polymer having a molecular weight between 150,000-600,000 g/mol and an average molecular weight which is higher than the average molecular weight of component (A1) but lower than the average molecular weight of component (A2) and a density controlled within the range of 910-960 kg/m.sup.3. Component B is produced separately from component A by using Ziegler-Natta or metallocene catalysts.

**BSPR:**

In EP-publication 129312 there is disclosed another similar polyethylene composition having three components, in which the product is formed from component (A) having a molecular weight between 50,000-500,000, component (C) having a molecular weight between 100,000-1,500,000 and component (B) having a molecular weight between 50,000-500,000 and being a homopolymer produced by a chromium catalyst. Components (A), (B) and (C) can be according to the publication manufactured as separate components or components (A) and (C) can together form a product prepared by a two-phase method, in which the weight ratio between components (A) and (A) is between 70:30-30:70. In the latter case the product can thus be considered a mixture formed from a unimodal product (B) and bimodal product (A/C).

**BSPR:**

In EP-publication 517222 it has also been disclosed a polyethylene product formed from an unimodal component and a bimodal component, which have been melt mixed together. In this case the product has been formed from 50-80 percent by weight of very high density polyethylene having a very broad molecular weight distribution, and from 20-50 percent by weight of LLD polyethylene or LD polyethylene having a melt index MFR.sub.2 between 0.5-2, and the product obtained is presented to be suitable for manufacturing pipes, sheets and films for low temperature conditions.

**BSPR:**

In bimodal products prepared by multiphase polymerization and containing low molecular weight polyethylene and high molecular weight polyethylene the processability can be essentially improved and molecular weight distribution can be controlled within a broad range. However, it has been found according to the invention that it is possible in certain way to improve the mixing of two phases having very different molecular weights and thereby the morphology and the processability of the products and the optimization of the mechanical properties. When essential improvements in processability and mechanical properties are tried to achieve, the phases of bimodal product have to be very different. This requires very accurate control of the phases.

**BSPR:**

Thus the invention concerns a polyethylene composition, which contains 85-99

percent by weight of a component (A) having a bimodal molecular weight distribution and a component (B) having an unimodal molecular weight distribution. Component (B) is a linear ethylene polymer having molecular weight between 150,000-600,000, a molecular weight distribution between 3.5-9.5, a melt index MFR.sub.21 between 0.5-10 and a density controlled within the range of 910-960 kg/m.sup.3, and the amount of component (B) calculated from the end product is between 1-15 percent by weight. The melt flow indices described herein have been determined at 190.degree. and the units are expressed as "g/10 min". MFR.sub.2, has been determined under a 21.6 kg load.

**BSPR:**

The polyethylene composition according to the invention is thus formed from two main components, the bimodal component of which has a bimodal molecular weight distribution. This component has the following general properties:

**BSPR:**

The polyethylene composition according to the invention can be prepared also by a multi-phase polymerization, in which for example in the first step an unimodal component is formed in amount corresponding of 1-15 weight-% of the end product and the bimodal component is formed in the second and the third polymerization step.

**BSPR:**

Further the polyethylene composition according to the invention can be prepared also so that a part of the fraction included in the low molecular weight fraction is added separately into the mixture formed by the bimodal component and unimodal component. The mixing is carried out preferably in an extruder, where the bimodal component and the unimodal polymer component are added in the beginning and a part, for example 1-50 weight-% of the component of low molecular weight is added as a side feed of the extruder. In this way it can be improved the homogeneity of the end product in the way described in Finnish patent application FI931343.

**DEPR:**

A bimodal polyethylene component A was prepared by a two-step process, in which the first step consisted of a loop polymerization and the second step consisted of a gas phase polymerization. The production rate of the loop reactor was 35-40 kg/h and the production rate of the gas phase reactor was the same. As a catalyst a Ziegler-Natta catalyst was used prepared according to Finnish patent application FI916192 by using Al-alkyl as cocatalyst. The catalyst was fed only into the loop reactor.

**DEPR:**

According to Example 1 a bimodal polyethylene was prepared so that the polymer fraction produced in the loop reactor having a high density (975 kg/m.sup.3) and a high melt flow (MFR.sub.2 =405) was introduced into a gas phase reactor in which the polymerization was continued for manufacturing bimodal product. 1-Butene was added into gas phase reactor as comonomer. The ratio between the components produced in the loop reactor and in the gas phase reactor was 50:50. The bimodal polyethylene obtained had the following properties:

**DEPR:**

According to Example 1 it was manufactured bimodal polymer so that the polymer fraction produced in the loop reactor and having a high density (975 kg/m.sup.3) and high melt flow index (MFR.sub.2 =450) was introduced into a gas phase reactor where the polymerization was continued for manufacturing a bimodal product. The ratio between the fractions produced in the loop reactor and in the gas phase reactor were 50:50. The bimodal product A5 obtained had the following properties:

**DEPL:**

The results indicate that with the compositions according to the invention it could be further improve ESCR-values compared with the only bimodal compositions in comparative tests 1 and 2. In experiment 5 into the bimodal polyethylene was added a homopolymer, which had been prepared by using chromium catalyst and the density of which was relatively high, e.g. 952 kg/m.sup.3. Also in this case the ESCR-value was essentially worse than the compositions according to the invention. The best stress cracking properties were achieved in experiment 5, in which a homopolymer was used.

## DEPL:

Due to greater melt flow index (MFR.sub.2) of the polymer fraction prepared in the loop reactor the ESCR-values of the end products were at higher levels as in Example 1. In spite of that the results indicate that when adding medium density copolymer it was achieved an essential improvement in the ESCR-values of the end product the addition amount being 10 weight-%.

## CLPR:

1. A polyethylene composition comprising 85-99.5 weight-% of component A, which is a linear (co)polymer of ethylene having a bimodal molecular weight distribution, comprising:

## CLPR:

2. A polyethylene composition according to claim 1, wherein the melt flow index determined under a 21.6 kg load or MFR.sub.21 of said component B is between 0.5 and 10 g/10 min.

## CLPR:

5. A polyethylene composition according to claim 1, wherein said bimodal Component A is formed of a first subcomponent, having a molecular weight between 5,000-50,000, a molecular weight distribution M.sub.w /M.sub.n between 2.5-9 and a melt flow index determined under a 2.6 kg load or MFR.sub.2 between 10-1,000 g/10 min, and a second subcomponent having a calculated molecular weight M.sub.W between 300,000-900,000 and a molecular weight distribution between 4.5-12.

## CLPR:

6. A polyethylene composition according to claim 5, characterized in that the melt flow index determined under a 2.16 kg load or MFR.sub.2 of said first subcomponent is between 150-500 g/10 min, and the density is between 950-980 kg/m.sup.3.

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L13: Entry 15 of 34

File: USPT

Jun 17, 1997

DOCUMENT-IDENTIFIER: US 5639834 A

TITLE: Process for producing polyethylene having a broad molecular weight distribution

## BSPR:

The present invention concerns a process for producing polyethylene having a broad molecular weight distribution. More particularly, the present invention relates to the production of high density polyethylene copolymers having a broad or bimodal molecular weight distribution.

## BSPR:

There is a demand for high molecular weight polyethylene, because an increase of the molecular weight normally improves the physical properties of the resins. However, high molecular weights tend to make polymers harder to process. On the other hand, an increase in the MWD tends to improve the flowability at high shear rate during the processing. Thus, broadening the MWD is one way to improve the processing of high molecular weight (=low melt flow index) polyethylene, in applications requiring fast processing at fairly high die swell, such as in blowing and extrusion techniques.

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L13: Entry 25 of 34

File: USPT

Sep 27, 1994

DOCUMENT-IDENTIFIER: US 5350817 A

TITLE: Process for the preparation of polyolefins having a broad molecular weight distribution

## ABPL:

Polyolefins having a molecular weight distribution  $M_{sub.w} / M_{sub.n}$  of  $\geq 3$  and which may be monomodal, bimodal or multimodal are obtained by polymerization or copolymerization of olefins of the formula  $RCH_2CH(R)R'$ , in which a catalyst system comprising an aluminoxane and a transition-metal component (metallocene) is used, the transition-metal component comprising at least one zirconocene of the formula I ##STR1## and at least one zirconocene of the formula Ia or alternatively at least 2 zirconocenes of the formula I.

## BSPR:

It is known that metallocene catalysts in combination with aluminoxanes are capable of polymerizing olefins to give polyolefins having a narrow molecular weight distribution ( $M_{sub.w} / M_{sub.n}$  of 2-3) (J. Polym. Sci., Pol. Chem. Ed. 23 (1985) 2117; EP-A 302 424). Polyolefins of this type with a narrow distribution are suitable, for example, for applications in precision injection molding, injection molding in general and for the production of fibers. For numerous applications, such as, for example, thermoforming, extrusion, blow molding and for the production of polyolefin foams and films, broader or bimodal molecular weight distributions are required.

## BSPR:

EP-A 310 734 proposes catalyst systems comprising a mixture of a hafnocene and a zirconocene for the preparation of polypropylene. Products have broad to bimodal distributions where  $M_{sub.w} / M_{sub.n}$  is from 3.7 to 10.3

## BSPR:

The object was thus to find a catalyst system and a process by means of which polyolefins having a broad, bimodal or multimodal distribution can be prepared and which avoid the disadvantages known from the prior art.

## BSPR:

The invention thus relates to a process for the preparation of a polyolefin which has a molecular weight distribution  $M_{sub.w} / M_{sub.n}$  of  $\geq 3.0$  and which may be monomodal, bimodal or multimodal, by polymerization or copolymerization of an olefin of the formula  $R_{sup.a}CH_2CH(R_{sup.b})R'$  in which  $R_{sup.a}$  and  $R_{sup.b}$  are identical or different and a hydrogen atom or a alkyl radical having 1 to 14 carbon atoms, or  $R_{sup.a}$  and  $R_{sup.b}$ , together with the atoms connecting them, can form a ring, at a temperature of from -60.degree. to 200.degree. C., at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst comprising a transition-metal component (metallocene) and an aluminoxane of the formula II ##STR2## for the linear type and/or of the formula III ##STR3## for the cyclic type, where, in the formulae II and III, the radicals R may be identical or different and are a C<sub>sub.1</sub>-C<sub>sub.6</sub>-alkyl group, a C<sub>sub.1</sub>-C<sub>sub.6</sub>-fluoroalkyl group, a C<sub>sub.6</sub>-C<sub>sub.18</sub>-aryl group, a C<sub>sub.1</sub>-C<sub>sub.6</sub>-fluoroaryl group or a hydrogen, and n is an integer from 0 to 50, or, instead of the aluminoxane, comprises a mixture of an aluminoxane of the formula II and/or of the formula III with a compound AlR<sub>sub.3</sub>, which comprises using, as the transition-metal component, at least one zirconocene of the formula I and at least one zirconocene of the formula Ia or alternatively at least 2 zirconocenes of the formula I ##STR4## in which  $R_{sup.1}$  and  $R_{sup.2}$  are identical or different and are a hydrogen atom, a C<sub>sub.1</sub>-C<sub>sub.10</sub>-alkyl group, a C<sub>sub.1</sub>-C<sub>sub.10</sub>-alkoxy group, a C<sub>sub.6</sub>-C<sub>sub.10</sub>

-aryl group, a C.sub.6 -C.sub.10 -aryloxy group, a C.sub.2 -C.sub.10 alkenyl group, a C.sub.7 -C.sub.40 -arylalkyl group, a C.sub.7 -C.sub.40 -alkylaryl group, a C.sub.8 -C.sub.40 -arylalkenyl group or a halogen atom,

**BSPR:**

The choice of the metallocenes for the polymerization of olefins to give polyolefins having a broad or multimodal distribution can take place by means of a test polymerization for each metallocene.

**DEPR:**

VN=267 cm.sup.3 /g, M.sub.w =293,000 g/mol, M.sub.w /M.sub.n =5.7, II=98.0%, MFI (230/5)=24.6 g/10 min.

**DEPR:**

VN=153 cm.sup.3 /g; M.sub.w =195,000 g/mol, M.sub.w /M.sub.n =5.8, II=96.0%, MFI (230/5)=87 g/10 min.

**DEPR:**

II=97.9%; MFI (230/5)=32 g/10 min, m.p.: 151.degree. C.

**DEPR:**

II=96.4%; MFI (230/5)=39 g/10 min; m.p.: 148.degree. C.

**CLPR:**

1. A process for the preparation of a polyolefin which has a molecular weight distribution M.sub.w /M.sub.n of .gtoreq.3.0 and which may be monomodal, bimodal or multimodal, by polymerization or copolymerization of an olefin, consisting essentially of propylene, at a temperature of from -60.degree. to 200.degree. C., at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst comprising a transition-metal component (metallocene) and an aluminoxane of the formula II ##STR12## for the linear type and/or of the formula III ##STR13## for the cyclic type, where, in the formulae II and III, the radicals R are identical or different and are a C.sub.1 -C.sub.6 -alkyl group, a C.sub.1 -C.sub.6 -fluoroalkyl group, a C.sub.6 -C.sub.18 -aryl group, a C.sub.1 -C.sub.6 -fluoroaryl group or hydrogen, and n is an integer from 0 to 50, or, instead of the aluminoxane, comprises a mixture of an aluminoxane of the formula II and/or of the formula III with a compound AlR.sub.3, which comprises using, as the transition-metal component, at least one zirconocene of the formula I and at least one zirconocene of the formula Ia or alternatively at least 2 zirconocenes of the formula I ##STR14## in which R.sub.1 and R.sub.2 are identical or different and are a hydrogen atom, a C.sub.1 -C.sub.10 -alkyl group, a C.sub.1 -C.sub.10 -alkoxy group, a C.sub.6 -C.sub.10 -aryl group, a C.sub.6 -C.sub.10 -aryloxy group, a C.sub.2 -C.sub.10 -alkenyl group, a C.sub.7 -C.sub.40 -arylalkyl group, a C.sub.7 -C.sub.40 -alkylaryl group, a C.sub.8 -C.sub.40 -arylalkenyl group or a halogen atom,

**CLPR:**

13. A process for the preparation of a monomodal, bimodal, or multimodal polyolefin having a molecular weight distribution M.sub.w /M.sub.n of .gtoreq.3.0, comprising:

**CLPR:**

15. A process for the preparation of a monomodal, bimodal, or multimodal polyolefin having a molecular weight distribution M.sub.w /M.sub.n of .gtoreq.3.0, comprising:

**CLPR:**

17. A process for the preparation of a monomodal, bimodal, or multimodal polyolefin having a molecular weight distribution M.sub.w /M.sub.n of .gtoreq.3.0, comprising:



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**Term:**

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